

Influence of the Stabilization System on the Rheological Behaviour of Plasticized PVC for Cables' Insulation

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Abstract

The paper is devoted to the rheological study of plasticized PVC - based compositions for cables' insulation, stabilized with three different systems (Ba laurate/Cd laurate, Sn dibutyl mercaptide, Pb bibasic stearate/Pb bibasic fosfite) in variable ratios. Starting from some measured parameters, several rheological properties - characteristic for the viscous and, respectively, elastic component of flowing - have been calculated (counter pressure, worm gear's rotation moment, shear stress at the wall, apparent viscosity, standard viscosity and the viscosity index, output pressure from the rheological nozzle, swelling, relaxation time, first function of the normal unitary stresses, index of elasticity). The observation to be made is that the system of thermal stabilization influences strongly the rheological behaviour by both its nature and amount, which requires a careful consideration of the effects, when products of different types are to be designed. The best thermal stabilization is assured by the Pb bibasic stearate/Pb bibasic fosfite - based system. The obtained recipes have been subsequently characterized from the viewpoint of their thermal stability and, equally, of some of their electrical properties. It was observed that the system of thermal stabilization strongly influences the thermal stability as well as the electrical properties of the plasticized PVC recipes. The highest values of thermal stability, which correlated with corresponding electrical properties, have been attained for the Pb- based system. When different stabilization systems are employed, the transparent, translucent or opaque insulations may be obtained.

Introduction

The considerable practical importance of plasticized poly(vinyl chloride) (PVC)-based compounds in the field of cables' insulation adds value to their rheological study [1,2]. As expected, it was observed that the addition of various compounds to the main polymer modifies the rheological properties to a considerable extent [2-4].

In the case of plasticized PVC melts, the rheological study is very complicated, as a result of the thermal sensitivity of this polymer, of its elastic component, and, equally, of the strong influence of the various additives (plasticizers, stabilizers, lubricants, flowing modifiers, etc.) that added to the main polymer so that the number of possible compositions becomes practically infinite [5,6,7]. The paper studies the rheological behaviour of some plasticized PVC based recipes, thermally stabilized with three different systems.

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Experimental

The rheological behaviour of 15 plasticized PVC-based compositions with a basic skeleton maintained permanently the same form was studied.

- PVC, K_w 70, 100 parts
- internal-external lubricant, 0.8 parts
- external lubricant, 0.2 parts
- co-stabilizer, epoxidated soy bean oil, 4 parts.

The recipes contain no internal lubricant, so that the compositions' gelling rate is not influenced.

The stabilizing systems of the three groups of recipes are formed as follows:

- *System I* - Ba laurate (BaL)/Cd laurate (CdL) (3/2 weight ratio), in the following ratios: 3, 3.5, 3.75, 4 and 4.5 parts for 100 g PVC;
- *System II* - Sn dibutyl mercaptide (SnM), in the following ratios: 3, 3.5, 3.75, 4 and 4.5 parts for 100 g PVC;
- *System III* - Pb bibasic stearate/Pb bibasic fosfite

(PbSP) (2.5/1.5 weight ratio), in the following ratios: 3, 3.5, 3.75, 4 and 4.5 parts for 100 g PVC.

The compositions' preparation involved dosing, mixing and granulating; among these operations, mixing evidenced a series of peculiarities worthy to be mentioned - as illustrated in Fig. 1.

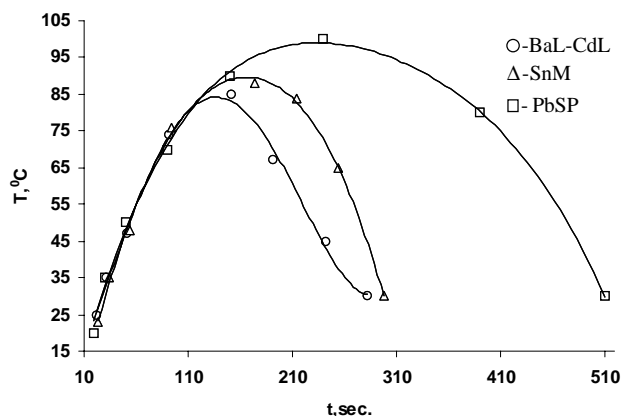


Fig. 1. Temperature variation with the mixing time, for the recipes with different stabilization systems.

The compositions have been tested on a laboratory extruder [8,9] especially equipped with devices for measuring counter pressure, the worm gear rotation moment, melt pressure and temperature along the cylinder, at 11D, 16D and 20D, respectively (where D is the cylinder diameter). The tests have been developed on a rheological nozzle with $L \times l \times h = 90 \times 20 \times 1$ mm characteristics. The extrusion head is equipped with a measuring ring, permitting a possible modification of the extrudate flow passing through it, and also permitting pressure's measurement.

The experimental program involved testing of 15 recipes, under temperature conditions ranging between 140 - 170°C, and a flow domain corresponding to the rotation speed ranging between 25 and 85 rpm.

Several parameters, such as the counter pressure exercised by the material occurring as a melt on the extruder various constructive parts, the rotation moment of the worm's gear during processing, the mass flow, the values of pressure in the region of the stabilized flow of the rheological nozzle, *etc.* have been measured. From the obtained by direct measurements data, the volume flow, the shearing stress at the wall and the shearing rate at the wall, the index of consistency or standard viscosity and apparent viscosity, the index of viscosity, the first and the second difference of the normal unitary stresses, the swelling, the elasticity coefficient, the relaxation time, the elasticity exponent were calculated.

Results and discussion

Analysis of temperature variation with the mixing time (Fig. 1) evidences that mixing of recipes stabilized with BaL-CdL and SnM is coincident with the ascending curve, and very close to the descending one. Mixing of recipes stabilized with PbSP derivatives is represented by the higher curve ($T=95^\circ\text{C}$) while mixing finishing occurs over a longer period of time.

Figure 2 plots graphically the variation of the counter pressure (C_p) as a function of the stabilizer's ratio for every stabilization system, and each of the seven values of rotation speed of the extrusion worm gear taken into analysis. It has been observed that, while the counter pressure exercised upon the extruder kinematical chain increases with rotation speed value in the case of processing recipes stabilized with BaL-CdL, it decreases with the recipes stabilized with SnM and remains approximately constant for recipes stabilized with PbSP.

In the case of recipes stabilized with BaL-CdL the variation of counter pressure with the ratio of stabilizer is linear on the whole domain of the values of rotation speed. For recipes stabilized with SnM, this is a second order polynomial function up to a value of 45 rpm, after which it becomes linear while, in the case of PbSP stabilized recipes, the variation is represented by a second order degree polynomial equation over the whole domain of values of rotation speed. It means that processing of the recipes stabilized with BaL-CdL is the most simple one; the extruder stressing increases when passing to the stabilization with PbSM.

Figure 3 (a, b) illustrates the variation of the worm gear's rotation moment (M_t), with the variation of the stabilizer ratio for the seven values of rotation speed. An increase of the rotation moment values is observed with the increase of rotation speed for recipes stabilized with BaL-CdL. For recipes stabilized with SnM it maintains at a practically constant value, while a decrease of the same parameter for the recipes stabilized with PbSP is observed (Fig. 3 a).

The variation of the rotation moment with the ratio of stabilizer at the same rotation speed is linear or very close to linearity in the case of recipes stabilized with BaL-CdL, and varies according to second-order polynomials with the other two stabilization systems - mainly with the PbSP containing ones (Fig. 3 b)

Figure 4 plots the variation of the shear stress, τ_p , with the real shear rate at the wall, γ_p , as well as with the stabilizer ratio. The difference between the two

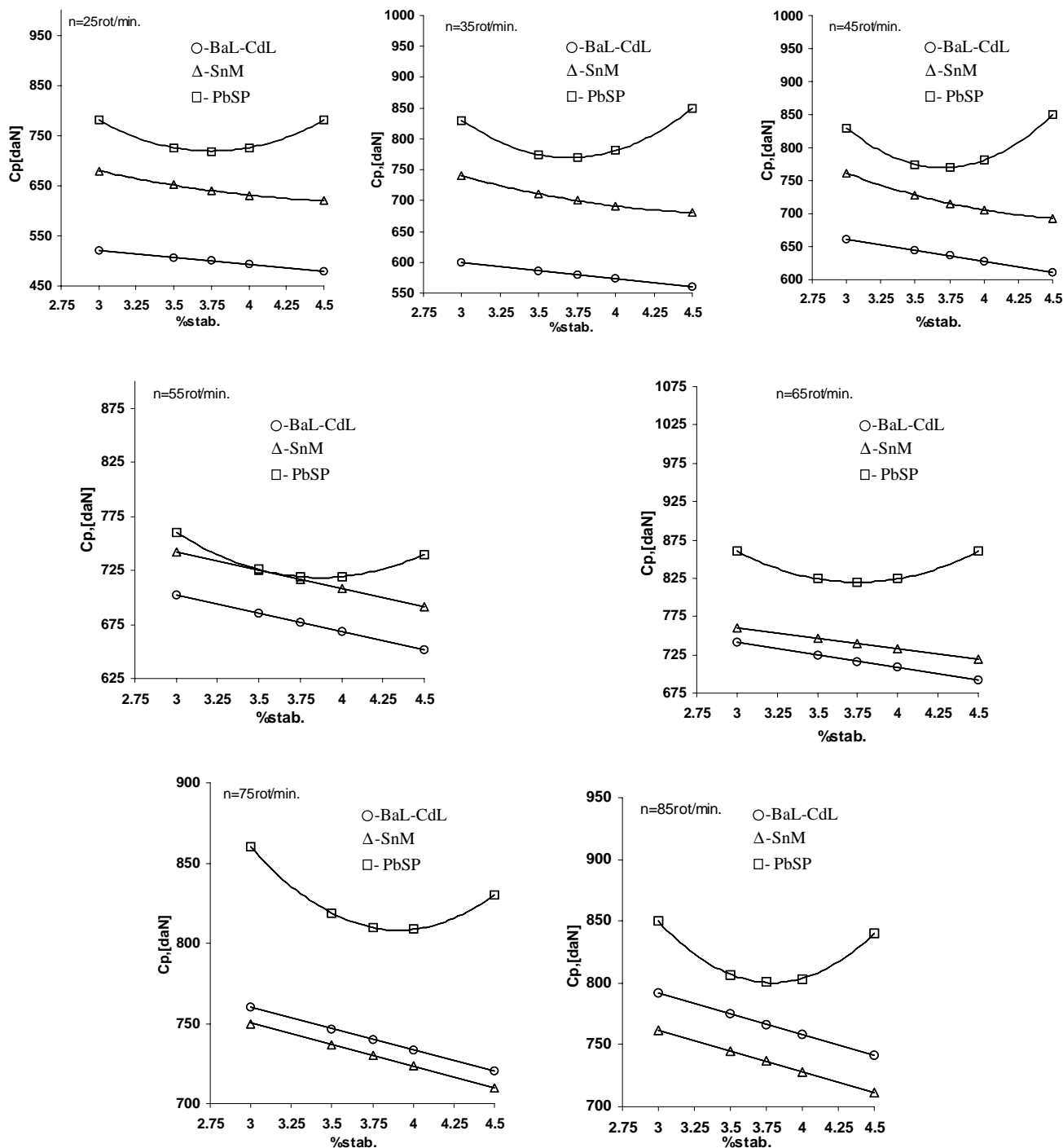
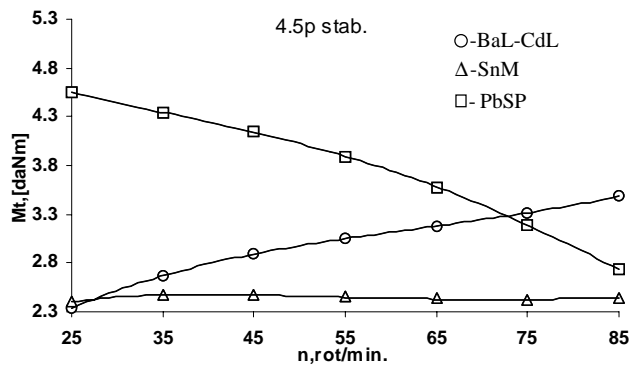
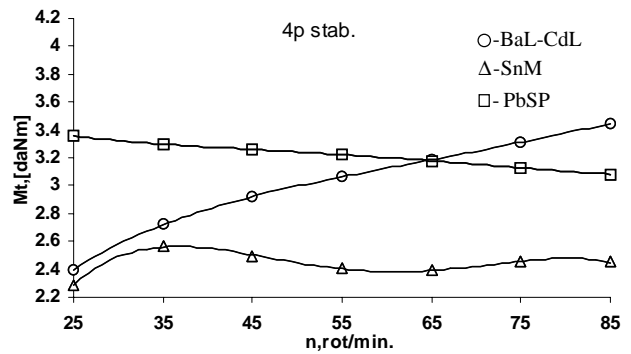
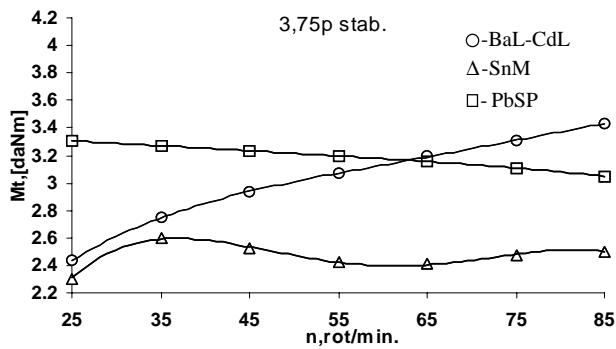
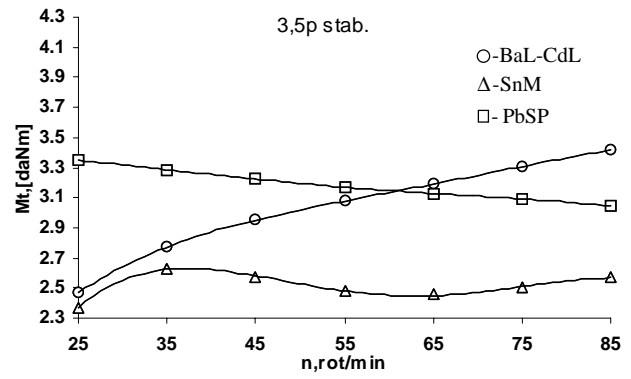
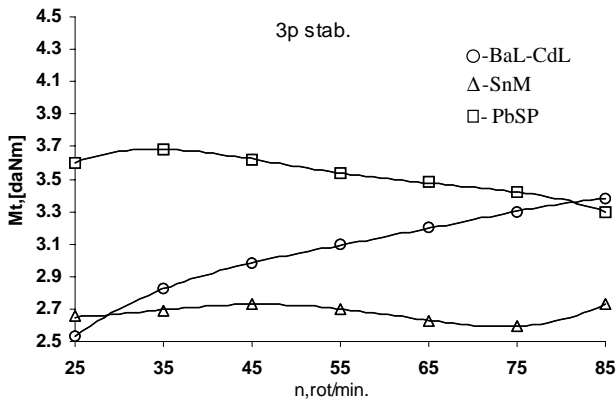


Fig. 2. The variation of the counter pressure as a function of the stabilizer's ratio for the three stabilization systems, for different values of the rotation speed of the extrusion worm gear.

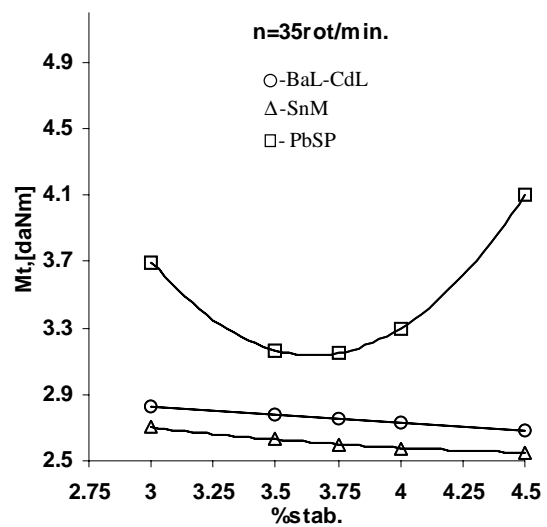
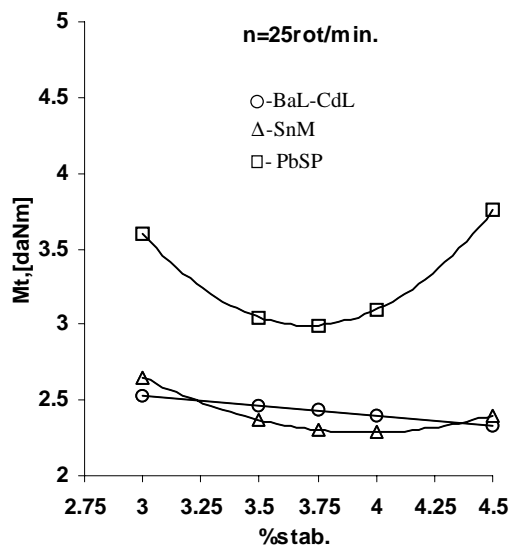
groups of graphs lies in the fact that, in the $\tau_p - \gamma_{ap}$ coordinates (a, c, e), the index of viscosity, n , is taken into consideration while, in the $\tau_p - \gamma_p$ diagrams (b, d, f), this parameter is neglected, which represents the other ones' precursory step. It was observed that the differences recorded between the flowing curves are the more pronounced the higher is the stabilizer ratio.

In the increasing direction of $\tau_p - \gamma_p$, the flowing

curves occur in the BaL-CdL, SnM, PbSP order. It has been also observed that, at shear rate higher than 150 s^{-1} and ratios of stabilizer of 4.5 parts for 100 parts of PVC, a reversal occurs in the position of the flowing curves for the recipes with BaL-CdL and SnM, *i.e.*, the recipes with 4.5 parts of BaL-CdL evidence a flow curve with a more pronounced slope than that of the recipe with 4.5 parts of SnM.



3a



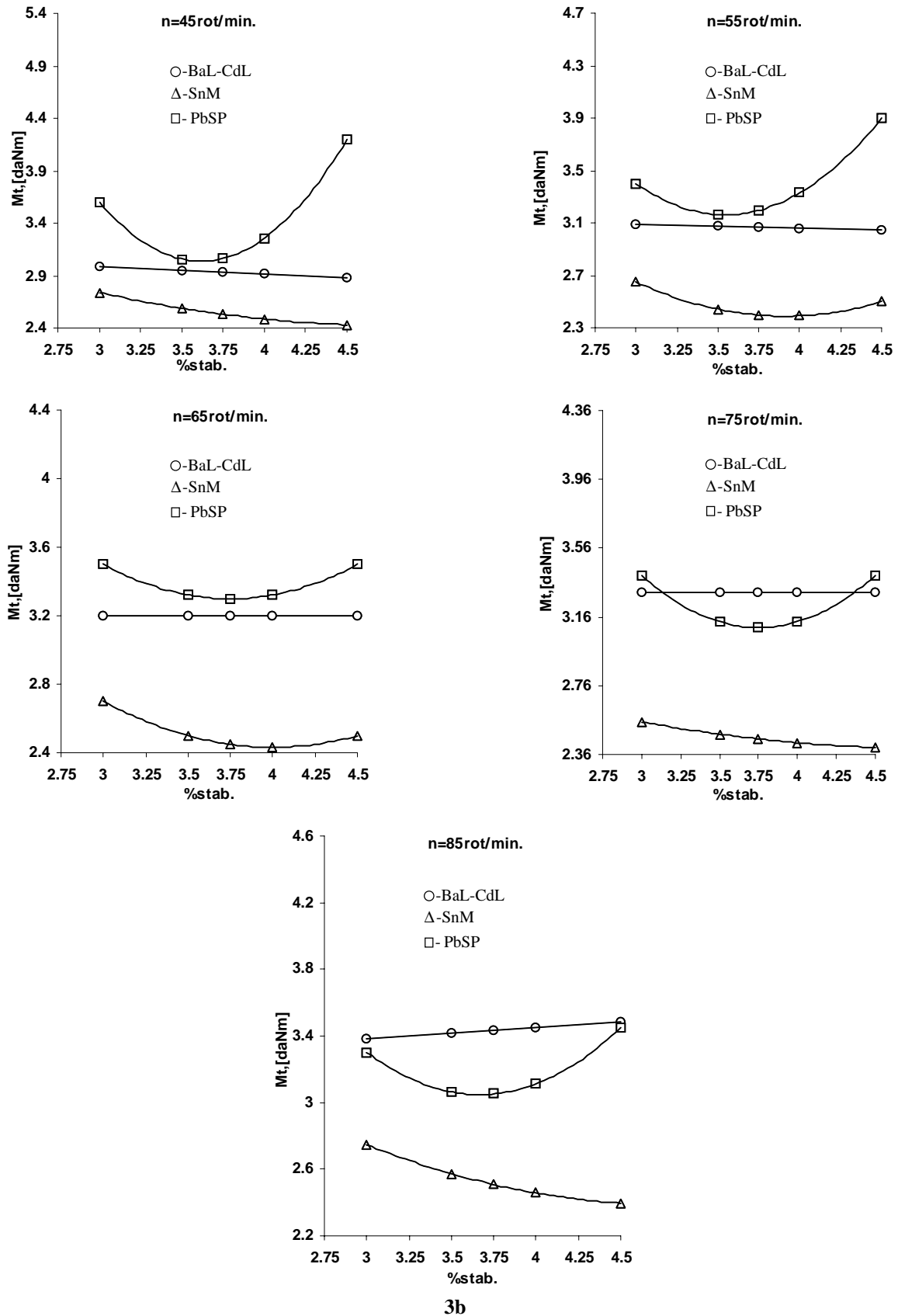


Fig. 3. The variation of the worm gear's rotation moment as a function of the rotation speed (for different values of the stabilizer's ratio, a) and of the stabilizer's ratio (for different values of the rotation speed of the extrusion worm gear, b), respectively.

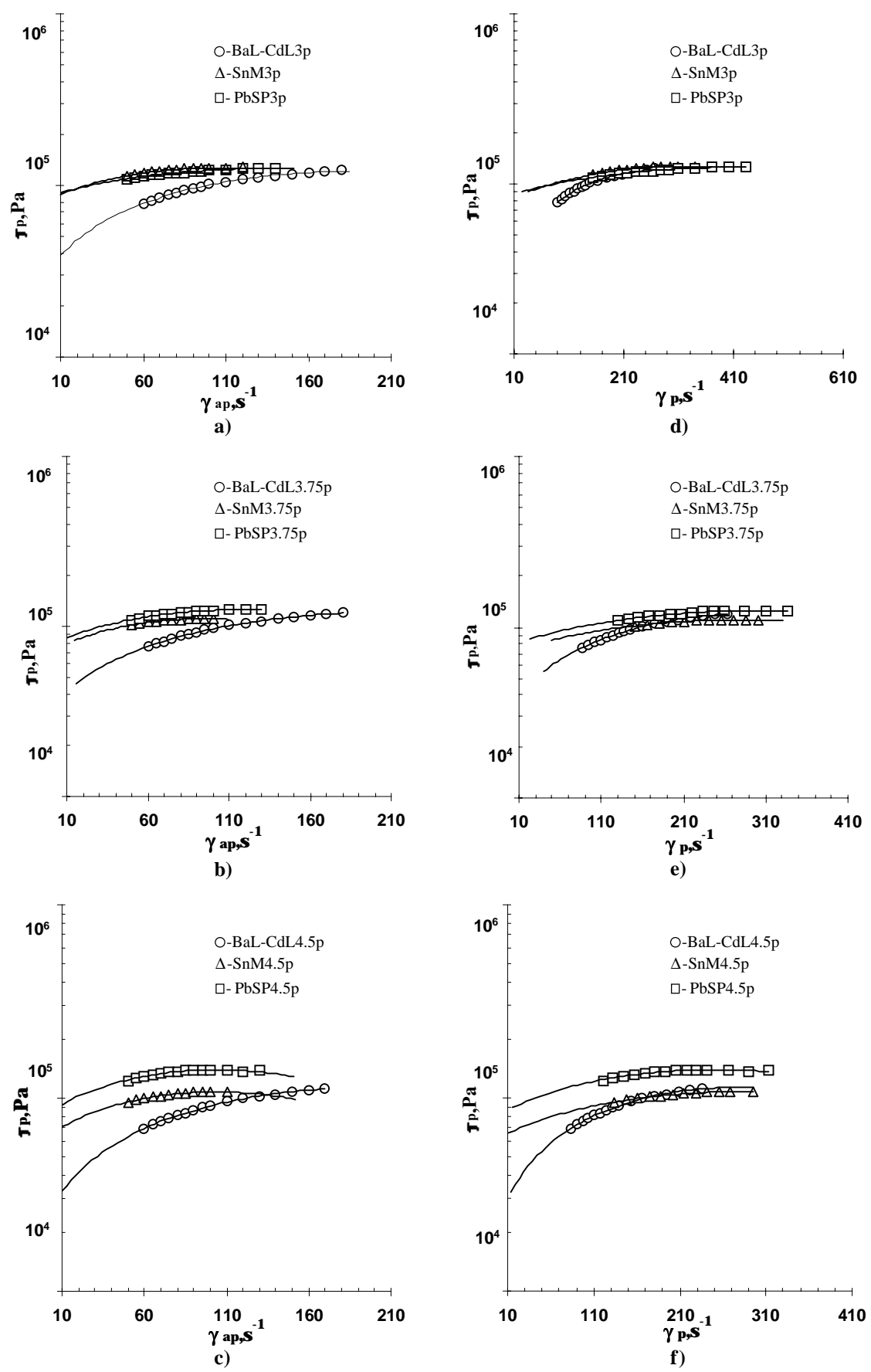


Fig. 4. The variation of the shear stress with the real shear rate at the wall, for different values of the stabilizer ratio.

The variation of apparent viscosity, η_a , as a function of the shear stress is plotted in Fig. 5, which evidences a clearcut differentiation among the three curves for each stabilizer ratio, the more so that the ratio of stabilizer increases.

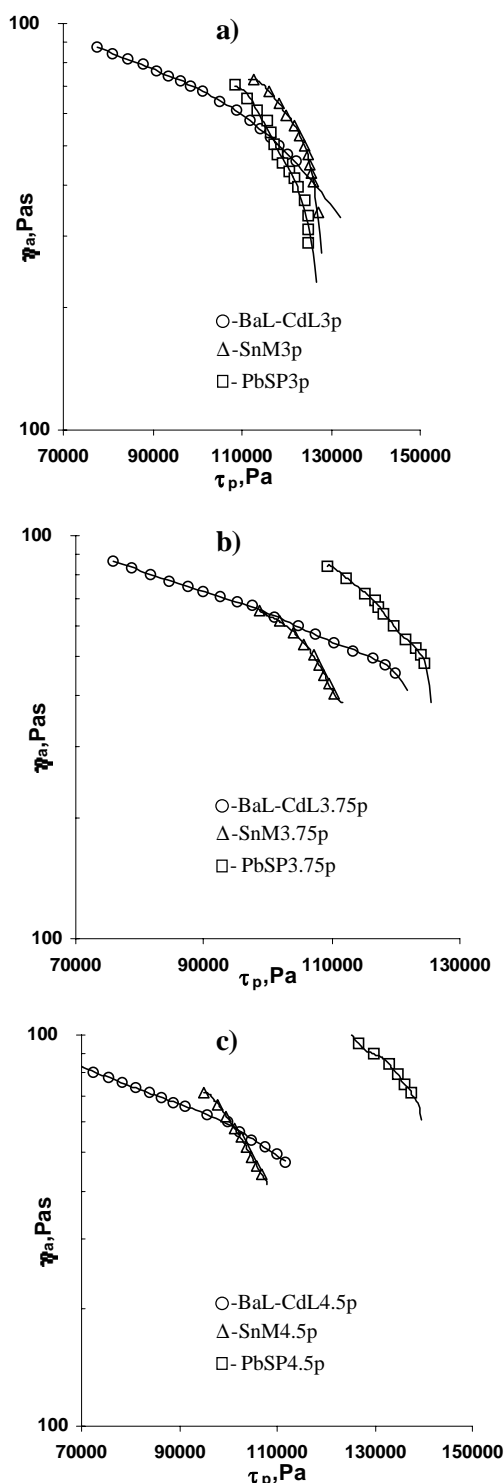


Fig. 5. The variation of apparent viscosity as a function of the shear stress at the wall, for different values of the stabilizer ratio.

The groups are seen as grouped in the case of recipes with 3 parts stabilizer and, respectively, dispersed with the increase of the stabilizer's ratio. The slopes of the tangents to the curves increase - for the same ratio of stabilizer - in the BaL-CdL<SnM<PbSP order, which signifies a reduction of the shear stress's influence on the variation of viscosity.

In parallel, Fig. 6 presents the standard viscosity (η_a^0) for each type of stabilizer, determined for a shear rate of 1 s^{-1} and the viscosity index, n [10,11]. One should observe the similarity between the shape and aspect of the curves drawn for BaL-CdL - and SnM stabilized recipes (concave); although they are differentiated through values (*e.g.* for the recipes stabilized with BaL-CdL, η_a^0 is lower with an order of magnitude than for those with SnM, while n is about 2.9 times higher for recipes with BaL-CdL than for those stabilized with SnM, and the curves appear as convex).

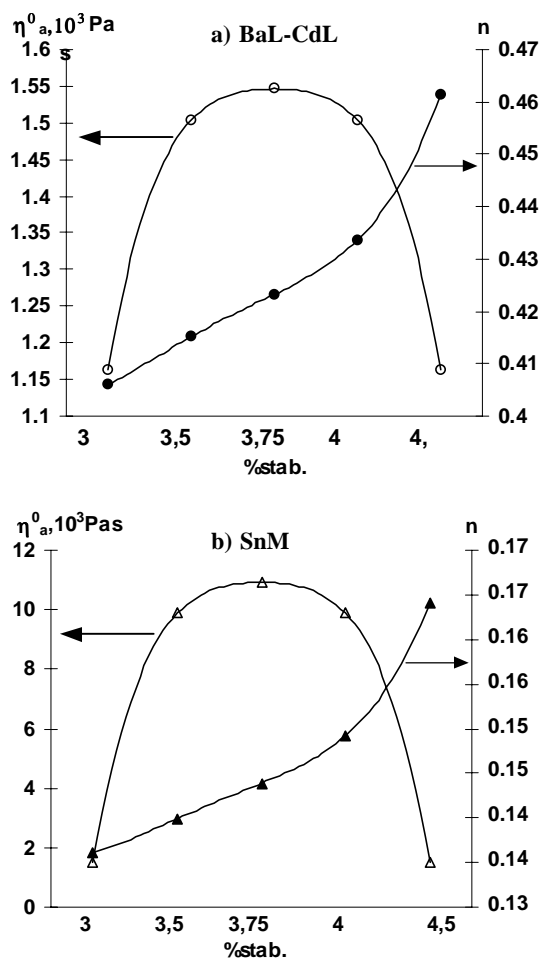


Fig. 6. The variation of the standard viscosity and the viscosity index, n , as a function of each type of stabilizer ratio, determined for a shear rate of 1 s^{-1} . a – BaL-CdL; b – SnM; c – PbSP.

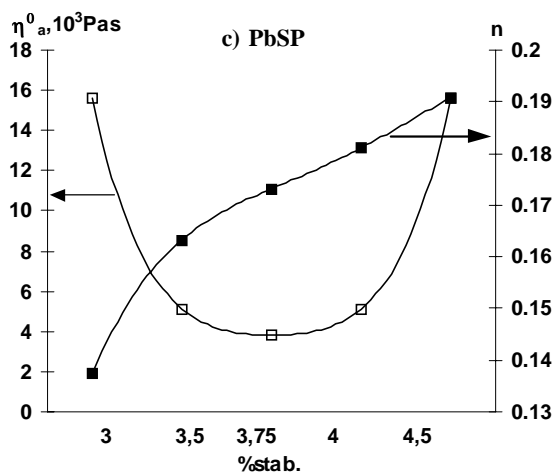


Fig. 6. Continued.

In the case of recipes stabilized with PbSP, the standard viscosity varies according to a convex curve, while the curve of the viscosity index takes a concave aspect.

As to the elastic behaviour of the 15 recipes, one may assert that it agrees with and completes the existing data on the viscous behaviour [12]. Thus, Fig. 7 illustrates the variation of the output pressure from the rheological nozzle, P_e , as a function of the shear rate at the wall, γ_p . The variation mode of this parameter - which is essential in the study of the elastic component - evidences a decrease of this one in the BaL-CdL>SnM>PbSP order, which is evidenced by the slopes and ordinates at the origin, of the curves defining functions.

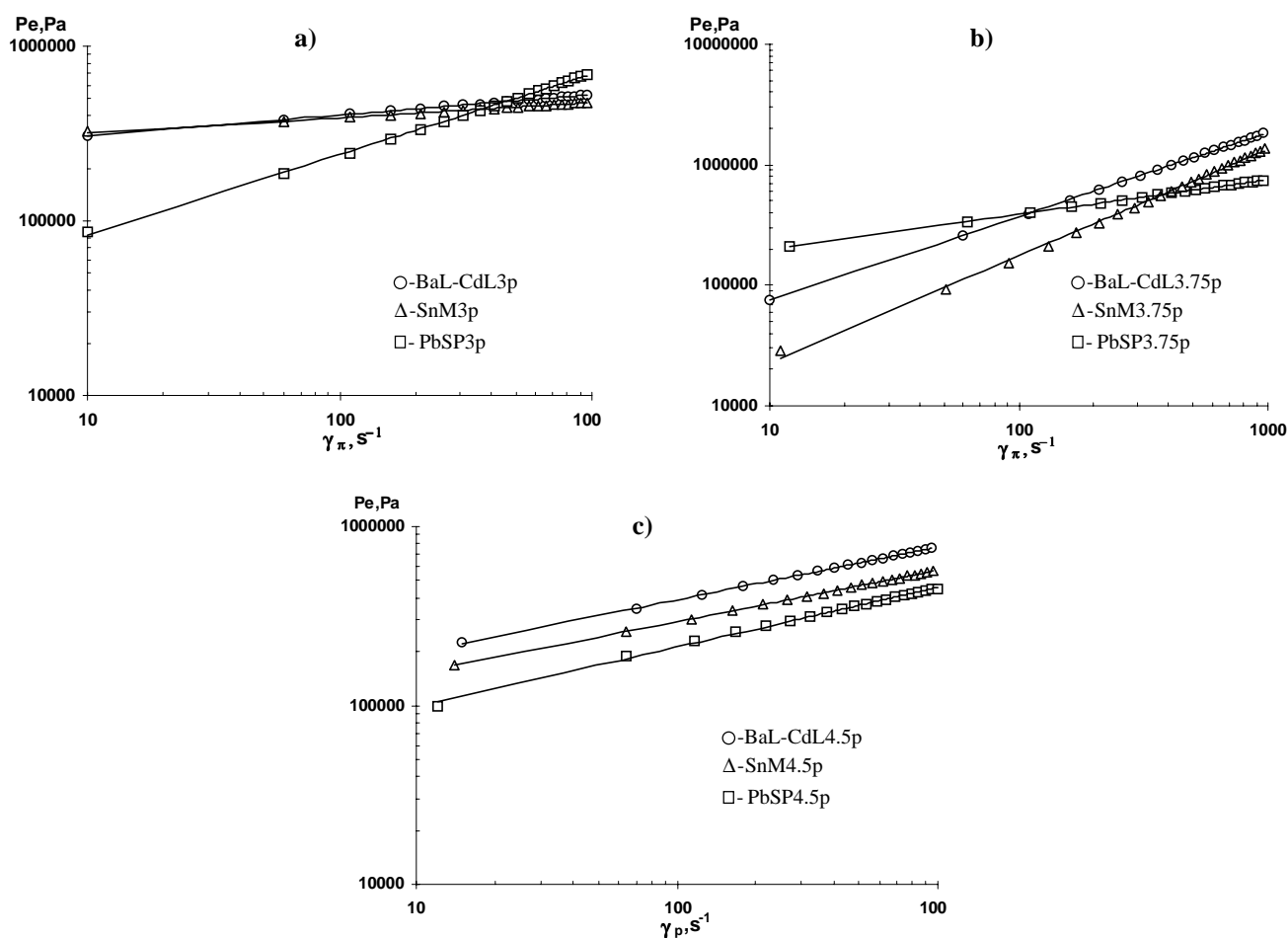


Fig. 7. The variation of the output pressure from the rheological nozzle as a function of the shear rate at the wall, for different values of the stabilizer ratio.

One should also observe that the recipes containing a PbSP stabilizer show - at all ratios - slopes that may be included between +30% and -9.4%, compar-

atively with the average of the three values. The slope's highest variation for the P_e curves is recorded with the recipes stabilized with SnM (*i.e.*, between

-34.12% and +112.75% versus the average value). Consequently, the P_e value of the recipes stabilized with SnM shows the highest dependence towards the shear rate at the wall, γ_p , while the recipes stabilized with PbSP show the lowest dependence.

By means of P_e , the first difference of the normal unitary efforts, N_1 , has been calculated and, from it,

the value of swelling, X , which represents the ratio between the extrudate's equivalent diameter and the equivalent diameter of the rectangular nozzle [13-15]. Swelling has been represented as a function of the shearing rate at the wall, γ_p , in Fig. 8, for different stabilizer ratios. The clear delimitation among the recipes is observed.

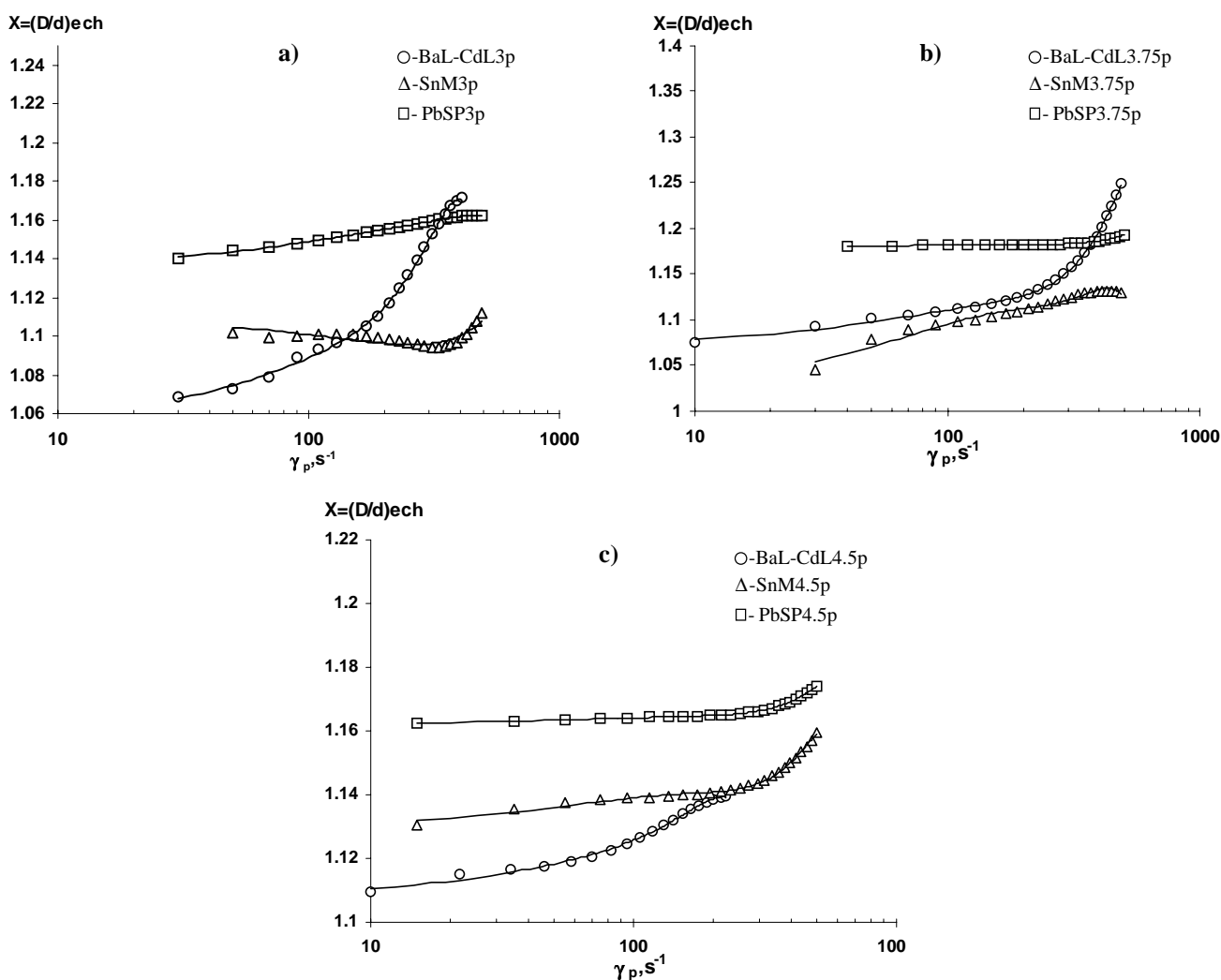


Fig. 8. The variation of the swelling as a function of the shear rate at the wall, for different values of the stabilizer ratio.

The tendency towards curves' linearization is observed with the increase of the stabilizer's ratio, while the recipes stabilized with PbSP evidence the highest dilatation values that should be considered in the design of devices for extrusion technologies.

Figure 9 plots graphically the variation of the relaxation time, θ , as a function of the shear rate at the wall, expressed logarithmically.

With the increase of the stabilizer ratio, the relaxa-

tion time decreases, a reversal occurring in the decreasing order, as follows: if, for a 3 parts stabilizer, the shortest relaxation time is recorded for the recipe stabilized with BaL-CdL, in the case of the 4.5 parts of stabilizer, it is the recipe stabilized with PbSP which shows the shortest relaxation time, due to the action of the PbSP itself, as a filling material.

The first function of the normal unitary stresses, ψ , and of the index of elasticity, m , as a function of

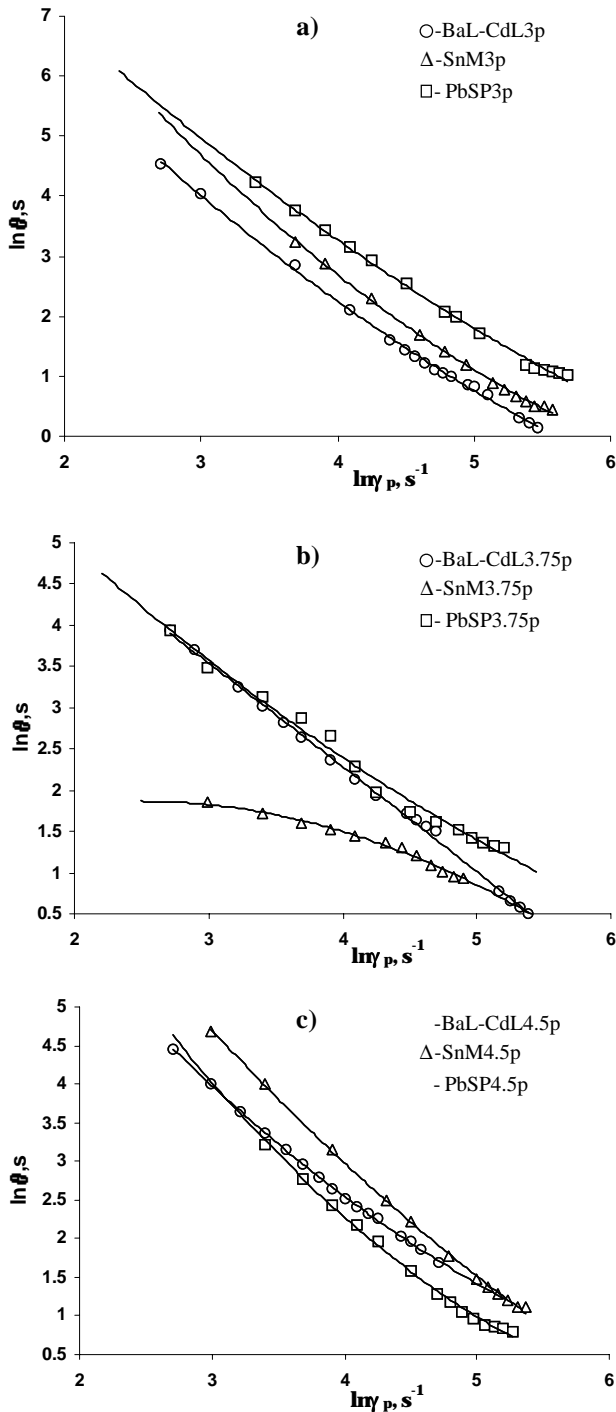


Fig. 9. The variation of the relaxation time as a function of the shear rate at the wall (expressed logarithmically), for different values of the stabilizer ratio.

the stabilizer ratio, is given in Figs. 10, 11.

All the three types of stabilizer determine standard elasticity functions, which evidence a minimum (Fig. 10) and also elasticity indices, showing a maximum at a 3.75 parts of stabilizer (Fig. 11), the order remaining the same: SnM, PbSP, BaL-CdL.

As to the main part of the stabilizer, that of assur-

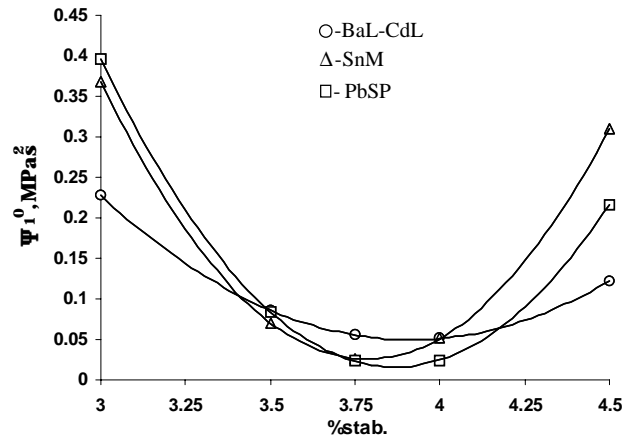


Fig. 10. The variation of the first function of the normal unitary stresses as a function of the stabilizer ratio, for the three stabilization systems.

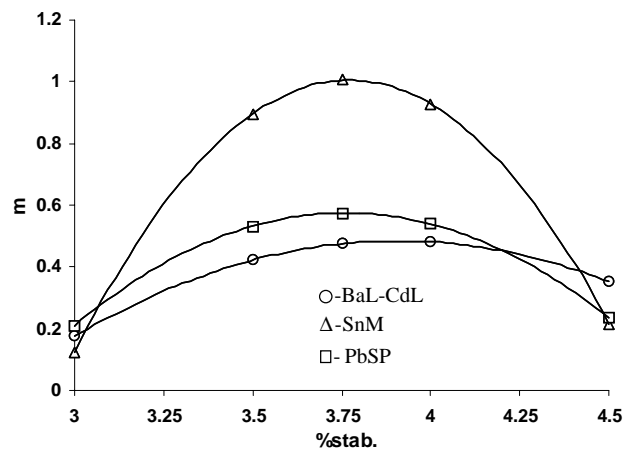


Fig. 11. The variation of the index of elasticity as a function of the stabilizer ratio, for the three stabilization systems.

ing the recipes stability during processing, the Fig. 12 plots the variation of the recipes time of the resistance, t , to the action of temperature (determination of stability with Congo red, at a temperature of $180^\circ C$), as a function of the stabilizer ratio.

Worth mentioning is the fact that, regardless of the ratio of BaL-CdL or SnM stabilizer, the resistance time is constant. In the case of recipes stabilized with SnM, stability's variation is constantly increasing and linear while, in the case of recipes stabilized with PbSP, thermal stability increases according to a second-order polynomial.

Bulk resistivity, defined as the ratio between the gradient of potential and the density of the current passing through the insulating material, has been represented in Fig. 13, as a function of the stabilizer's ratio.

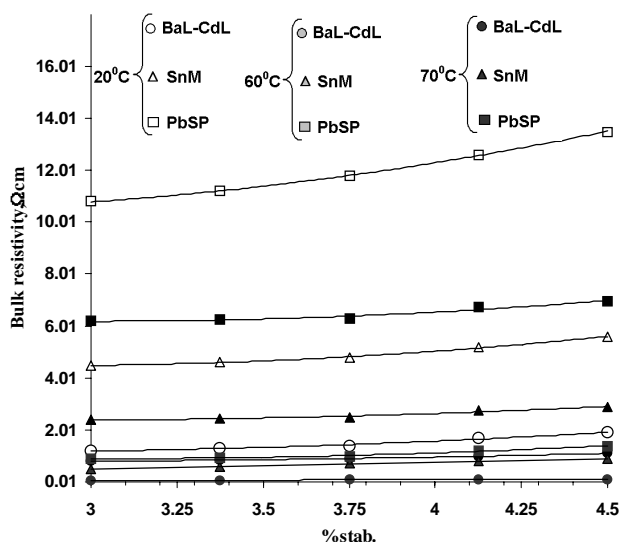


Fig. 13. The variation of the bulk resistivity as a function of the stabilizer ratio, for different temperatures.

This characteristic is seen as being influenced both by the stabilizer ratio and by temperature. Determinations with the 15 recipes have been performed at three temperatures, as follows: 20, 60 and 70°C. The results show that, from the viewpoint of their bulk resistivity, the recipes stabilized with a PbSP stabilizer have been most strongly influenced, followed by those stabilized with SnM, the least influenced ones being the recipes stabilized with BaL-CdL.

On the other hand, the recipes stabilized with PbSP show the highest values of bulk resistivity at 20°C, the values recorded decreasing at half at 60°C and then decreasing again 6 times, at 70°C.

Bulk resistivity is least influenced by temperature in the case of the recipes stabilized with BaL-CdL. Special mention should be made here of the polynomial variation of the curves with relatively low slopes of the tangents.

Figure 14 illustrates the variation of the tangent of the dielectric losses angle, $\text{tg}\delta$, at frequency 50 Hz, as a function of the stabilizer ratio.

Again, one should notice the influence of the stabilizer type and of temperature. This time, the highest increase of the tangent values have been recorded - with the increase of the stabilizer ratio- for stabilization with PbSP and SnM, while, the most significant decrease of the tangent's value are observed for recipes stabilized with PbSP and especially with BaL-CdL, when temperature increases from 60°C to 70°C.

Conclusion

The system of thermal stabilization of plasticized

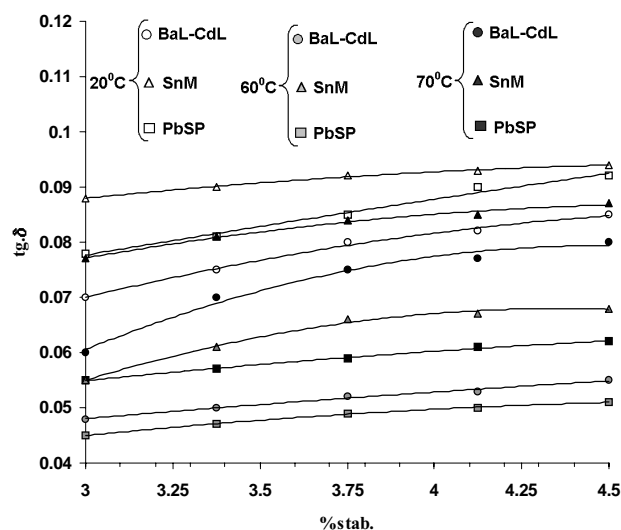


Fig. 14. The variation of the tangent of the dielectric losses angle (at a frequency of 50 Hz), as a function of the stabilizer ratio, for different temperatures.

PVC influences considerably the recipes rheological behaviour, which requires a careful consideration of the effects, when products of different types are to be designed.

The best thermal stabilization is assured by the PbSP - based system.

The system of thermal stabilization influences the electrical properties of the plasticized PVC recipes.

When different stabilization systems are employed, the transparent, translucent or opaque insulations may be obtained.

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